Kerr Orientation Influence on Excited State Absorption Measurements

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Z. Naturforsch. **41 a,** 983–985 (1986);
received February 8, 1986

The possible influence of a strong nonresonant laser field on the orientation of dyes in solution is discussed as a potential source of measuring errors in excited state absorption analysis. The results of investigations on some typical samples suggest that, fortunately, the effect is very small.

Optical pumping of molecules with non-isotropic transition moments by laser light, polarized or nonpolarized, always produces a non-isotropic distribution in the excited state. Besides the selective excitation, an orientation of the molecules by the strong laser field could occur via the Kerr effect, as is well known for CS_2 (see e.g. [1]). For calculations of the excited state cross section from the probe beam absorption, the angular-dependent population density has to be evaluated. In two cases the problem can be solved very easily: i) If the orientational decay time τ_{rot} and the excitation pulse with Δt_{pulse} are much shorter than the excited state lifetime τ_{L}, the excited state population will be isotropic after a delay time $\gg \tau_{\text{rot}}$, Δt_{pulse}. This method is usually applicable for triplet state measurements and sometimes for singlet measurements too (especially with ps-measurements). ii) If the fluorescence scaling method [2] can be used, the population density will be known, provided the polarizations of the probe light and fluorescence light are made identical before detection. In all other cases a more detailed analysis is necessary. Much work has been done to investigate the non-isotropic excitation effect to obtain fluorescence [3], ground state recovery, excited state absorption, vibrational relaxation [7, 8, 15] and inhomogeneous broadening [15] data (e.g. [3–17]. According to [6], the effect of non-isotropic excitation can be considered in a simple way by using the "magic" angle of 54.7° between the polarization directions of the excitation and the probe light. But this is useful only in the case of a small excited state population (population density of the excited state $n_1 \propto$ excitation intensity: I_{exc}). Fortunately, the maximum relative error amounts to about n_1/n_{total}. The additional orientation of the molecules by the optical Kerr effect (e.g. [1]) is in the small density approximation at least proportional to I_{exc}, which yields an $n_1 \propto I^2_{\text{exc}}$ dependence of the excited state population.

For measuring this orientational change of some common solutions, ground state absorption changes were detected in the presence of a strong, linearly polarized, nonresonant laser field. The strong light was produced (see Fig. 1) by a ns-Nd-glass laser (1060 nm, 1.7 J, 20 ns), horizontally polarized by a set of Brewster angle plates and focussed by a 100 mm lens to an averaged beam waist diameter of 3 mm. The average intensity of $1.2 \cdot 19^9\ \text{W/cm}^2$ was chosen to be below the "break through point" in the sample of 10 mm thickness. The first "sparks" were detectable with the photomultiplier earlier than visually. The vertically polarized probe light of 530 nm was generated in a detuned KDP crystal. Using perpendicular polarization for the probe beam, we could avoid the influence of other high intensity effects on our measurements. With the beamsplitter (glass plate) the reference signal of the probe light was taken out, filtered and detected with the photodiode (PD). The 1060 nm light was blocked in front of the photomultiplier (PM) with an interference filter and coloured glass filters. The sum of the reference signal (PD) and the electrically delayed probe signal (PM) was registered with a storage oscilloscope (Tektronix 7834, 7A19, 400 MHz). To obtain the transmission without the strong field, the 1060 nm light was blocked with coloured glass filters (4 mm BG18, Schott) at position F1. Bleaching effects by the 530 nm light were excluded. The solutions had to be exchanged between shots (one per 5 min) for reproducible results. Damage of the sample windows (simple glass plates) led to a remarkable change in transmission. All measurements were made at room temperature. The compounds Rhodamine 6G, Oxazine 1 (Oxazine 725), DODC-I (all from Lambda Physik), Rubrene and Cresylviolet (Merck), DNS (Diamino-nitro-stilbene, home made) and the solvents (Merck, fluorescence spectroscopic) were used without further purification.

The results are given in the Table 1. The absorption coefficient α was calculated from the transmission T and the length of the cuvette L:

$$\alpha = -\frac{1}{L}\ln T \quad \text{with} \quad T = \frac{I_{\text{s}}}{I_{\text{ref}}}. \tag{1}$$

$\Delta\alpha$ is the difference of the absorption coefficients with and without the 1060 nm light, which turned out to be mostly determined by the statistical measuring error. Although each result is derived from 10 good shots of each kind, the deviations are not small.

The theoretical description of these measurements is possible under the assumption of a linearly polarized excitation field. Steady state conditions ($\tau_{\text{rot}} \ll t_{\text{pulse}}$) lead to the following Boltzmann distribution function $f(\theta)$ of the population density:

$$f(\theta) = \frac{1}{Q}\exp\left\{\frac{\tilde{A}\boldsymbol{E}^2\cos^2\theta}{2kT}\right\},$$

$$Q = \int_0^{2\pi}\int_0^{\pi} \exp\left\{\frac{\tilde{A}\boldsymbol{E}^2\cos^2\theta}{2kT}\right\}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi. \tag{2}$$

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* Died June 20th, 1985.

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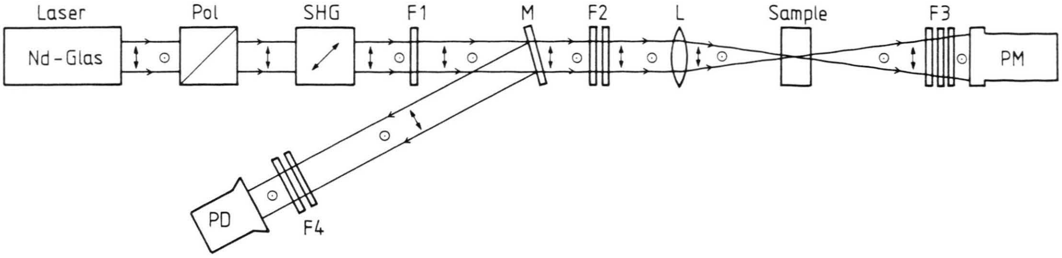

Fig. 1. Experimental arrangement. Pol: Brewster angle glass stack polarizer, SHG: KDP-Kristal (530 nm generation), F1 ... F4: Filters, M: glass plate, L: lens with 100 mm focal length, PM: Photomultiplier, PD: Photodiode, polarization directions ↕ horizontally, ⊙: vertically.

Table 1.

Compound	Solvent	Conc. $/ \frac{\text{mol}}{\text{l}}$	τ_{rot} [ps]	$\Delta\alpha/\alpha$	$A / \frac{\text{K}}{\text{W}}$
Rhodamine 6G	Ethanol	$4.2 \cdot 10^{-6}$	270 [11] 255 [13]	$< 10\%$	$2.4 \cdot 10^{-8}$
Rubrene	Benzene	$2.6 \cdot 10^{-4}$		$< 3\%$	$7.3 \cdot 10^{-9}$
Cresylviolet	Ethanol	$1.1 \cdot 10^{-4}$		$< 7\%$	$1.7 \cdot 10^{-8}$
Oxazine 1	Ethanol	$1.7 \cdot 10^{-3}$		$< 8\%$	$2.0 \cdot 10^{-8}$
DODC-I	Ethanol	$9 \cdot 10^{-5}$	50 [18] and [6]	$< 6\%$	$1.5 \cdot 10^{-8}$
DNS	o. Dichlorobenzene	$9 \cdot 10^{-4}$	$\cong 1000$ [9]	$< 2.2\%$	$5.4 \cdot 10^{-9}$

The angle θ describes the orientation of the molecular dipoles in relation to the electric field vector $\boldsymbol{E}$, and $\tilde{A}$ is the interaction constant.

With $C = \frac{\tilde{A}\boldsymbol{E}^2}{2kT} \ll 1$ the approximation $\exp(C\cos^2\theta) \cong 1 + C\cos^2\theta$ leads to

$$Q = 4\pi\left(1 + \frac{\tilde{A}\boldsymbol{E}^2}{6kT}\right) = 4\pi\left(1 + \frac{C}{3}\right). \tag{3}$$

The Lambert Beer law becomes

$$I(x) - I(x + \mathrm{d}x) = \int_0^{2\pi}\int_0^{\pi} \sigma n_{\text{total}} f(\theta) \cos^2\theta \sin\theta \,\mathrm{d}\theta \,\mathrm{d}\varphi \tag{4}$$

with the assumption that the transition dipole moment has the same direction as the main polarizability. With $C \ll 1$ we get

$$\frac{T(I_{\text{exc}})}{T(I_{\text{exc}} = 0)} = \exp\left\{-\left(\frac{1 + 3C/5}{1 + C/3} - 1\right)\alpha L\right\} \tag{5}$$

with $T(I_{\text{exc}} = 0) = \exp(-\alpha L)$ or, again using $C \ll 1$,

$$\frac{T(I_{\text{exc}})}{T(I_{\text{exc}} = 0)} = \exp\left\{-\frac{4}{15} C\alpha L\right\} = \exp\left\{-\frac{4}{15}\frac{\tilde{A}\boldsymbol{E}^2}{2kT}\alpha L\right\}. \tag{6}$$

From (1) we obtain

$$\frac{\Delta\alpha}{\alpha} = \frac{4}{15}\frac{\tilde{A}\boldsymbol{E}^2}{2kT}, \tag{7}$$

$$\frac{\Delta\alpha}{\alpha} = \frac{A}{T} \cdot I_{\text{exc}}. \tag{8}$$

Using the last equation, the upper limits of the new interaction constant A for the different solutions were calculated and are given in the table. Excited state absorption measurements were usually carried out with excitation intensities of 100 MW/cm^2 or less. This would result in a relative difference for the population density smaller than 10^{-2} according to our results. Fortunately, deviations of that size can usually be neglected.

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Erratum

Claus Kahlert, Existence and Uniqueness of Solutions of Piecewise-Defined Continuous Dynamical Systems, Z. Naturforsch. **41 a,** 567.

Part (b) in the subscription of Fig. 1 must be complete as follows:

(b) A dissipative oscillator possessing a limit cycle. Here

$$\tau^1 = \{(x, y)^{\mathrm{T}}\ x > 0,\ |y| < x\}\,, \qquad F^1(x, y) = (\varrho(1 - x), 1)^{\mathrm{T}}\,;$$

$$\tau^2 = \{(x, y)^{\mathrm{T}}\ y > 0,\ |x| < y\}, \qquad F^2(x, y) = (-1, \varrho(q - y))^{\mathrm{T}}\,;$$

$$\tau^3 = \{(x, y)^{\mathrm{T}}\ x < 0,\ |y| < -x\}, \qquad F^3(x, y) = (-\varrho(1 + x), -1)^{\mathrm{T}}\,; \quad \text{and}$$

$$\tau^4 = \{(x, y)^{\mathrm{T}}\ y < 0,\ |x| < -y\}, \qquad F^4(x, y) = (1, -\varrho(1 + y))^{\mathrm{T}}\,.$$

For $\varrho < 1$ …"?